

CHEMICAL DESULFURIZATION OF COAL TO MEET POLLUTION CONTROL STANDARDS

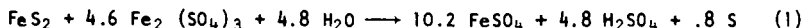
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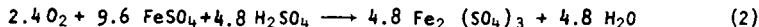
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INTRODUCTION

The Meyers' Process is a new approach⁽¹⁾ for meeting federal and state sulfur oxide emission standards for coal-fired electric utilities. The process removes up to 80% of the sulfur from coal through chemical leaching of pyritic sulfur with aqueous ferric sulfate solutions at temperatures of 50°-130°C (eq 1).



The leaching agent is regenerated at similar temperatures using oxygen (eq 2).



and sulfur and iron sulfates are removed as reaction products. The selectivity for pyrite is high with little or no reaction of the reagents with the coal matrix being found for Appalachian coal.

Although only pyritic sulfur is removed (organic bound sulfur remains), the Meyers' Process has wide applicability for converting US coal reserves to a sulfur level consistent with governmental standards for sulfur emissions from power plants and industrial sources. Samples from coal mines in Montana, through Iowa, Illinois, Ohio, Pennsylvania, West Virginia and Kentucky, representing a wide range of US production and reserves have been desulfurized to meet these standards utilizing the Meyers' Process (Environmental Protection Agency Contract 68-02-0647). Physical cleaning has generally been unable to accomplish similar sulfur reductions for the coals tested without severe coal reject losses. Because of the relatively high pyritic sulfur and low organic sulfur contents of Appalachian coals (70% of current US coal production), the process appears to have major impact in this area.

The concept of chemically removing pyrites from coal has not heretofore been thought practical as a solution to the sulfur oxide air pollution problem, even though it is well known that pyrites may be oxidatively converted to soluble sulfates by strong oxidizing agents such as nitric acid, hydrogen peroxide or chlorine. These oxidizing agents are not seriously advanced as the bases of processes for lowering the sulfur content of coal as they also seriously oxidize the coal matrix. Furthermore, nitric acid nitrates coal and chlorine greatly increases the chlorine content of coal. A number of groups^(2,3) have investigated the use of hot alkali, but have abandoned this approach presumably because much of the input base reacts with coal silicates, aluminates and the organic matrix, causing excessive reagent and coal losses.

Aeration of coal in aqueous suspension has often been suggested for conversion of the pyritic sulfur content of coal to a soluble sulfate, as it is known that the mechanism of acid mine drainage involves slow conversion of pyrite to soluble sulfate. However, attempts to speed up this process under favorable conditions of air supply, temperature and fineness of coal have only resulted in a reduction of residence time to weeks or months rather than years⁽²⁾. Thus, it was not thought possible to devise a practical process for chemically removing or dissolving the pyritic sulfur content of coal.

Bench-scale tests of more than 200 ferric solution extractions and 50 leach solution regenerations have been performed to date (Environmental Protection Agency Contract EHSD 71-7) for the purpose of defining reaction kinetics. A typical expression for pyritic sulfur removal from (from Lower Kittanning coal) is⁽⁴⁾:

$$r_L = \frac{-d[W_p]}{dt} = K_L W_p^2 Y^2 = \text{wt of pyrite removed/100 wts of coal/hour} \quad (3)$$

where,

W_p = weight percent pyrite in coal,

Y = ferric ion to total iron weight ratio in leacher, and

$K_L = A_L \exp(-E_L/RT)$, a function of temperature and coal particle size,

and for ferric regeneration⁽⁴⁾:

$$r_R = \frac{-d[Fe^{+2}]}{dt} = K_R [O_2][Fe^{+2}]^2 = \text{moles of ferric ion regenerated per unit time,} \quad (4)$$

where,

$[O_2]$ = oxygen partial pressure in atmospheres,

$[Fe^{+2}]$ = ferrous ion concentration in moles/liter, and

$K_R = A_R \exp(-E_R/RT)$, a function of temperature only.

Experimental results for both Meyers' Process extraction and float sink testing (physical cleaning) of nineteen US coals are presented in the following section.

RESULTS

One-ton run-of-the-mine coal samples, representing at least one day's production were collected from each of 19 coal mines by Commercial Testing and Engineering Company of Chicago, Illinois. The coal mines were selected to provide information on a wide variety of coal beds and regions with special emphasis on the Appalachian Basin. The coal analysis summary (Table 1) shows that the coals range from sub-bituminous A through low volatile bituminous in rank, in total sulfur from 1.0 to 6.4%, and in pyritic sulfur from 0.3 to 5.2% w/w (dry, moisture-free basis).

TABLE 1
COAL ANALYSIS SUMMARY^a

Region	Seam	State	Mine	As Received Basis		Dry Forms of Sulfur, % w/w				Dry Proximate Analysis, % w/w			
				Rank	Moisture % w/w	Total	Pyritic	Sulfate	Organic	Ash	Volatiles	Fixed Carbon	Heat Content Btu/lb
Appalachian Coal Basin	Sewickley Meigs Creek No. 9	Penn Ohio	Narwick Muskingum	hVAb	1.50	1.37	1.09	0.01	0.27	40.47	27.77	31.76	8612
				hVAb	3.36	6.08	3.65	0.06	2.37	21.68	36.36	41.96	11014
	Pittsburgh	Penn	Mathies	hVAb	1.67	1.46	1.05	0.04	0.37	41.01	24.53	34.46	8154
	Pittsburgh W. Va.		Humphrey No. 7	hVAb	1.63	2.58	1.59	0.01	0.98	9.88	37.66	52.46	13631
	Pitts. No. 8	Ohio	Egypt Valley No. 21	hVAb	2.07	6.55	5.07	0.14	1.34	25.29	36.12	38.59	10594
	Pitts. No. 8	Ohio	Powhatan No. 4	hVAb	2.10	4.12	2.57	0.19	1.36	37.17	29.01	33.82	8603
	U. Freeport	Penn	Delmont	hVAb	0.77	4.89	4.56	0.08	0.25	27.18	28.33	44.49	11012
	U. Freeport	Penn	Jane	hVAb	1.17	1.85	1.44	0.00	0.41	21.75	30.07	48.18	11932
	Freeport	Penn	Marion	hVAb	2.21	1.37	0.90	0.02	0.45	26.40	25.45	48.15	11046
	Middle Kittanning Lower	Penn	Lucas	hVAb	3.89	1.79	1.42	0.05	0.32	8.68	35.30	56.02	13451
Eastern & Western Interior Coal Basins	Kittanning Lower	Penn	Bird No. 3	lvb	0.84	3.14	2.87	0.05	0.22	30.23	16.18	53.59	10550
	Kittanning Lower	Penn	Fox	hVAb	1.82	3.82	3.14	0.04	0.64	13.55	38.33	48.12	12973
	Kittanning Clarion 4A	Ohio	Meiggs	hVAb	4.77	3.73	2.19	0.06	1.48	26.53	34.92	38.55	10246
	Mason	E. Kentucky	No. 1 ^b	hVAb	2.22	3.12	1.98	0.08	1.06	11.39	38.91	40.70	13054
	Illinois No. 5	Illinois	Eagle No. 2	hVAb	3.31	4.29	2.64	0.04	1.61	26.53	34.30	39.17	10566
	No. 9	W. Kentucky	Camp No. 1 & 2	hVAb	3.99	4.51	2.80	0.06	1.65	21.13	35.86	43.01	11105
	Herrin No. 6	Illinois	Orient No. 6	hVAb	3.51	1.66	1.30	0.01	0.36	22.51	31.67	45.82	11163
	Des Moines No. 1	Iowa	Meldon	hVAb	13.29	6.39	5.24	0.15	1.00	15.74	40.62	43.64	11760
	Rosebud	Montana	Colstrip	subA	20.41	1.01	0.34	0.00	0.67	10.38	43.09	46.53	11591

^aAll values are the average of triplicate determinations.
^bDixie Fuel Company.

Because of the widespread application of physical cleaning techniques for removal of non-combustible rock (which includes varying amounts of pyrite) from coal (along with some carbon), float-sink fractionation was performed to define the relative utility for each coal of washing and chemical desulfurization. The summary chart (Table 2) of pyritic sulfur removal results shows that a) the Meyers' Process, at its current state of development, removes 83-98% of the pyritic sulfur content of the 19 coals studied, resulting in total sulfur content reductions of 40 to 82%, b) nine of the coals are reduced in sulfur content to the 0.6 - 0.9% sulfur levels generally consistent with the federal standard for new stationary sources and many state standards, while two coals are reduced below 1.0% sulfur by physical cleaning, c) with the exception of the Jane and Lucas mines, the Meyers' Process removes significant to very large increments of sulfur over that separable by physical cleaning, and d) in one case, the Mathies mine, coal cleaning results in a sulfur content increase.

State emission regulations for discharge of sulfur oxides from utility and large industrial power plants⁽⁵⁾ can also be met by application of the Meyers' Process. The Pennsylvania state standard for eight air basins is approximately 1.1% sulfur, for coal of 25mm btu/ton. The Marion, Mathies, Bird No.3 and Delmont mines all meet this standard after chemical desulfurization but do not meet the standard after efficient physical cleaning. These coals could also be transported to New Jersey or New York to meet their state standards of approximately 1.0%, and 1.8 and 2.4% sulfur, respectively. The Meigs and Powhatan No.4 mines would meet the '28 county standards' of approximately 2% sulfur for the state of Ohio after treatment by the Meyers' Process, whereas efficient cleaning of these coals reduces their sulfur content to only 2.8 and 3.3%.

The Camp mine in western Kentucky meets the state standard for 'Priority 3' regions of less than 2.3% sulfur after treatment by the Meyers' Process, whereas physical cleaning reduces the total content of this coal to 2.9%. The Humphrey No.7 mine is reduced to 1.5% sulfur, which meets the West Virginia standards for 'Regions 2 and 3' of 1.7 and 2% respectively, whereas physical cleaning reduces the sulfur content to 1.9%. The Weldon mine in Iowa is reduced to 2.3% sulfur by the Meyers' Process which meets the state requirement of approximately 3.1% sulfur. Physical cleaning does not meet the standard, reducing the sulfur content to 3.8%.

We feel that process improvements such as more efficient residual sulfur and sulfate removal and especially utilization of physically cleaned coal will cause most coals to be further reduced in sulfur content to the '95% removal' level shown in Column 4 of Table 2.

In commercial practice for production of clean fuel, it is very likely that an optimum process cost and product will be obtained by cleaning coal prior to ferric sulfate leaching, to remove rock and some of the larger pyrite particles. There are preliminary indications that the efficiency of the Meyers' Process may be enhanced by utilization of physically cleaned coal.

TABLE 2
SUMMARY OF PYRITE REMOVAL RESULTS
COAL SURVEY PROGRAM

Mine	% Total Sulfur w/w in Coal ^{a,b}			Meyers Process Pyrite Conversion % w/w	Meyers Process Total Sulfur Decrease % w/w	% Sulfur in Coal ^d After Efficient Coal Cleaning
	Initial	After Meyers' Process				
		Current Results	95% Removal ^c At			
1. Colstrip	1.0	0.7	0.7	83	40	e
2. Warwick	1.4	0.8	0.3	92	43	1.0
3. Marion	1.4	0.7	0.5	94	50	1.2
4. Mathies	1.5	0.9	0.5	98	44	1.7
5. Jane	1.8	0.7	0.5	91	61	0.8
6. Orient No.6	1.7	0.9	0.4	96	47	1.4
7. Lucas	1.8	0.9	0.4	92	50	0.7
8. Humphrey No.7	2.6	1.5	1.1	91	42	1.9
9. No. 1	3.1	1.6	1.2	90	48	2.3
10. Bird No. 3	3.1	0.8	0.4	95	74	1.5
11. Fox	3.8	1.6	0.8	89	58	2.0
12. Meiggs	3.7	1.9	1.6	93	49	2.8
13. Powhatan No.4	4.1	2.0	1.7	84	51	3.3
14. Camp	4.5	2.0	1.8	96	56	2.9
15. Eagle No. 2	4.3	2.0	1.8	94	51	2.9
16. Delmont	4.9	0.9	0.6	98	82	2.1
17. Muskingum	6.1	3.2	2.6	93	48	4.4
18. Egypt Valley	6.6	2.7	1.7	93	49	4.6
19. Weldon	6.4	2.2	1.4	98	66	3.9

^aDry, moisture-free basis.

^bExperimental conditions are shown in the Experimental Section. ^d1.90 float material, 14x0 mesh is defined here as the limit of efficient coal cleaning.

^cSulfur content of coal at 95% pyrite removal, and no increase in sulfate or measured organic sulfur content.

^eFloat-sink testing was not run on this coal due to its low ash and pyrite content.

A more detailed coal analysis summary for coals tested by the Meyers' Process is shown in Table 3. These results show that a) a measured heat content rise of up to 5 - 10% is obtained for the Appalachian and some of the Interior Basin coals, while on a dry mineral matter and pyrite heat content free basis, heat content changes are essentially negligible as to be expected for negligible reaction of the coal organic matter, b) the Colstrip (western) and Orient No.6 (eastern interior) coals show small heat content losses, c) ash removal, in addition to that accounted for by pyrite decrease was observed in varying degrees for all coals, d) an increase in organic sulfur content in excess of that for ash removal occurs for some coals while small decreases occur for others.

As the Appalachian Basin provides most of the US coking coal production, it was deemed desirable to obtain free swelling index (FSI) data on these coals. Actual coke-oven testing is, of course, required to obtain assurance of retention of coking properties after Meyers' Process treatment. FSI values of 4 - 8 measured for the Appalachian coals showed no significant change after processing.

EXPERIMENTAL METHOD

Chemical Removal of Pyritic Sulfur.

The general conditions for pyritic sulfur removal have been adapted from the bench-scale studies⁽⁴⁾ with the objective of obtaining 90% - 100% pyritic sulfur removal and of simulating process design as nearly as possible, consistent with efficient laboratory operations.

Mesh Size - coal ground to 100 mesh x 0 or finer has been found to give high extraction rates and to be most satisfactory for laboratory scale sampling, although coal top sizes up to -1/4" have been tested and give reasonable although reduced reaction rates.

Ferric Ion Concentration - ferric sulfate solution 1N in ferric ion appears to be optimum, although differences due to concentration change do not appear to be great.

Reaction Temperature - the reaction temperature was held at the reflux temperature of 1N ferric sulfate solution which is approximately 102°C. This allows a reasonably high reaction rate and yet does not require pressure equipment.

Reaction Time - each coal was leached a total of 10 - 24 hours depending on the characteristics of the individual coal being treated.

Ferric Ion to Total Iron Ratio⁽⁴⁾ - since the rate of pyrite removal is slowed substantially by ferrous ion accumulation (see eq 3), each coal was treated under conditions designed to keep $\bar{Y} > 0.80$ by one of the following means:

TABLE 3
TREATED COAL ANALYSIS SUMMARY^a

Region	Seam	Mine	Dry Forms of Sulfur, % w/w					Dry Proximate Analysis, % w/w					
			Total	Pyritic	Sulfate	Organic	% Pyrite ^b Removal	Ash	Volatiles	Fixed Carbon	Heat Content btu/lb	Content Change %	
Appalachian Coal Basin	Sewickley Meigs Creek No. 9	Warwick Muskingum	0.82 3.22	0.09 0.27	0.14 0.17	0.59 2.78	92 93	35.32 16.05	26.61 36.95	38.07 47.00	9365 11587	8.7 5.2	
	Pittsburgh Pittsburgh Pitts. No. 8	Mathies Humphrey No. 7 Egypt Valley No. 21	0.94 1.49 2.71	0.02 0.14 0.38	0.10 0.10 0.13	0.82 1.25 2.20	98 91 93	36.43 6.97 18.69	25.51 37.04 38.08	38.05 55.93 43.23	9024 13949 11533	10.7 2.3 8.9	
	Pitts. No. 8	Powhatan No. 4	2.04	0.43	0.12	1.49	84	32.12	29.28	36.60	9430	9.6	
	U. Freeport Jane Freeport	Delmonta Marion	0.90 0.69 0.68	0.11 0.14 0.05	0.05 0.06 0.06	0.74 0.49 0.57	98 91 94	20.14 17.99 22.62	29.95 30.36 25.31	49.91 51.65 52.07	12150 12417 11720	10.3 4.1 6.1	
	Middle Kittanning Lower	Lucas	0.89	0.20	0.12	0.57	92	6.32	35.15	58.53	13883	3.2	
	Kittanning Lower	Bird No. 3	0.80	0.16	0.11	0.53	95	24.17	17.57	58.25	11493	8.9	
	Kittanning Clarion 4A	Fox Meigs	1.64 1.94	0.37 0.16	0.09 0.14	1.18 1.64	89 93	9.72 20.39	38.31 35.27	51.97 44.34	13174 10582	1.5 3.3	
	Hason	No. 1	1.62	0.21	0.09	1.32	90	8.50	37.63	53.87	13341	2.2	
	Illinois No. 5	Eagle No. 2	2.04	0.19	0.23	1.62	94	19.49	34.62	45.89	11428	6.5	
	Western Interior Coal Basins	No. 9 Herrin No. 6 Des Moines No. 1	Camp No. 162 Orient No. 6 Weldon	2.02 0.93 2.25	0.14 0.06 0.15	0.16 0.17 0.12	1.72 0.73 1.98	96 96 98	15.27 18.25 5.94	36.45 31.92 -	48.28 48.83 -	11740 11034 12735	5.7 1.2 8.3
	Western	Rosebud	Colstrip	0.69	0.06	0.06	0.57	83	5.17	42.45	52.38	11321	2.3

^aAll values are the average of duplicate or triplicate runs.

^bBased on before-and-after weight of pyrite present.

- Increasing the solvent to coal ratio (w/v) from a nominal 10 to a maximum of 40
- Changing the leach solution after 3 - 6 hours of reaction or more often if required
- A combination of the above.

Post Sample Treatment - after treatment, the samples were thoroughly washed to remove any residual leach solution and then dried. All sample calculations were done on a dry basis in order to eliminate variables due to wetness of the coal. Sulfur forms and proximate analysis have been obtained for each treated coal sample.

The exact procedure is described below:

One hundred grams of 100 mesh x 0 coal were added to 2-l refluxing 1N ferric sulfate solution contained in a 4-necked 3-l glass cylindrical reaction vessel equipped with a mechanical stirrer, reflux condenser and a thermocouple attached to a recorder. Each vessel also had a stopcock at the bottom for taking samples and was heated by a specially constructed heating mantle. After the coal addition, an additional 0.5-l 1N ferric sulfate solution was used to wash down the sides of the vessel. At this point, the t_0 solution sample was taken and the leaching process was considered started. Then, the reaction mixture, which was at $88 \pm 4^\circ\text{C}$, was rapidly brought to reflux, a process that takes 8 - 12 minutes. Leach solution samples for each iron analysis were taken by drawing a 200 ml aliquot of the reaction mixture from which a 20 ml sample was taken and cooled immediately to 0°C . Unused material was returned to the reaction flask. After cooling, a 14 ml aliquot was centrifuged to remove all suspended solids and 10 ml of this was used for iron analysis. Any remaining coal or leach solution was returned to the reaction flask.

After 4 - 6 hours when Y was reduced to approximately 0.8, the heating was stopped and the reaction mixture was drained from the flask, filtered and sucked as dry as possible. The final reaction volume and approximate solvent retention on the coal were then determined. The wet, unwashed coal was then slurried with 200 ml fresh ferric sulfate solution at 30°C and added to 2-l fresh 1N ferric sulfate solution at reflux. Another 300 ml ferric sulfate was used to wash any residual coal into the flask. A t_0 leach solution sample was taken immediately and the entire reaction mixture was brought to reflux in 8 - 12 minutes. Leach solution samples were taken at regular intervals, and after a total elapsed reaction time of 10 to 24 hours, the reaction mixture was drained from the reaction flask, filtered and washed clear with 0.5-0.1-l water.

The extracted coal was slurried with 2-l of water or 1N sulfuric acid of $\sim 80^{\circ}\text{C}$ for 2 hours, filtered and then stirred with another 2-l at $\sim 80^{\circ}\text{C}$ for an additional two hours. After filtration, this procedure was repeated with 2-l water at $\sim 80^{\circ}\text{C}$. If scheduling did not permit coal to be extracted with toluene immediately, it was stirred at $\sim 50^{\circ}\text{C}$ for an extended period until it would be filtered and extracted.

After the extraction of residual sulfate and iron, the wet coal was transferred into a 1-l round bottom flask equipped with a mechanical stirrer and Dean-Stark trap. Then 400 ml toluene was added and the mixture was brought to reflux. This was continued until all the water was azeotroped off (approximately 0.75 - 1.25-hr and 50 - 75 ml) plus another 15 minutes. The hot solution was then filtered, washed with 50 - 75 ml toluene, and then dried in a vacuum oven at 100 - 120 $^{\circ}\text{C}$. This coal was then weighed and analyzed.

FLOAT-SINK TESTING (Commercial Testing & Engineering Co.)

Five hundred pounds each of the 1-1/2" x 100 mesh, 3/8" x 100 mesh and 14 mesh x 0 portions obtained from the initial sampling of the coals were fractionated according to standard float-sink procedures using organic liquids of 1.30, 1.40, 1.60 and 1.90 specific gravities. Head samples for each size (or grind), each gravity portion and the two 100 mesh x 0 samples were analyzed on a dry basis for % w/w ash, total sulfur and pyritic sulfur. The raw data was then used to calculate washability data showing cumulative recovery and cumulative reject at the various specific gravities for each of the size portions.

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